CEMF.ir
Center of Engineering
Multiscale Modeling
Fluid Flow

Aspen Plus®
HDPE Production Process

Simulation of HDPE slurry phase reactor using Aspen Plus®

Compatible with
Aspen Plus® v10 or Higher

Authors
Alireza Bahrami
Hamid Reza Norouzi

Amirkabir University of Technology

Center of Engineering and Multiscale Modeling of Fluid Flow

Extra consideration:

- This document is developed to teach how to use the software. The document has gone under several reviews to reduce any possible errors, though it may still have some. We will be glad to receive your comments on the content through this address: h.norouzi@aut.ac.ir

Document history

Revision	Description	Date
Rev. 1.00	Final changes and refinements.	09-Jan-2021
Rev 0.02	Final draft was prepared.	03-Dec-2020
Rev 0.01	The tutorial was reviewed and commented	01-Dec-2020
Rev 0	The first draft was prepared.	23-Nov-2020

Table of Contents

Title **Page**

Problem Definition

Consider a stream with the specified composition in Table 1 at pressure 200 KPa and temperature 358.15 K that enters the reactor as feed for the HDPE production process. The slurry phase reactor model is CSTR and operates at803.51 kPa. Volume of the reactor is 30.60 m^3 and there is a thermodynamic equilibrium between the vapor and the slurry phase. Simulate the reactor and calculate the molecular mass distribution of the polymer (HDPE) in the reactor exit.

Table1. The values of the components involved in the process

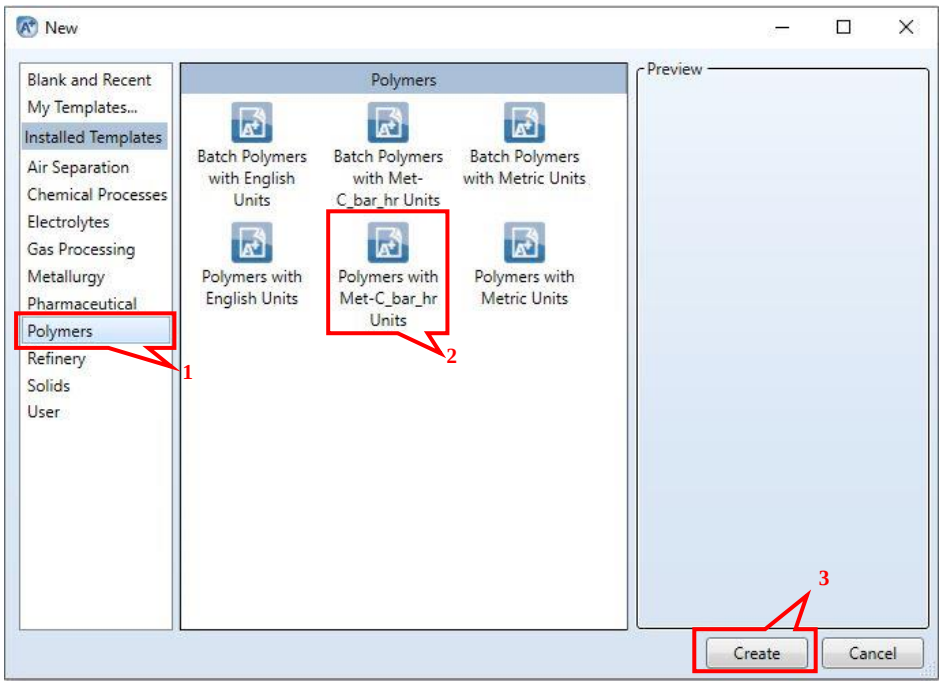
Component	Mass flow rate [kg/hr]
Titanium tetrachloride (Catalyst)	8.99
Triethylaluminium (Co-catalyst)	8.99
Ethylene (Monomer)	5999.70
Hydrogen (Chain transfer agent)	0.3
n-Hexane (Solvent)	53982

Note: You can find the simulation file this flowsheet online on www.cemf.ir alongside this tutorial file.

Solution

New simulation

1. Start a new Aspen Plus® simulation with **Polymers with Met_C bar_hr Units** template.

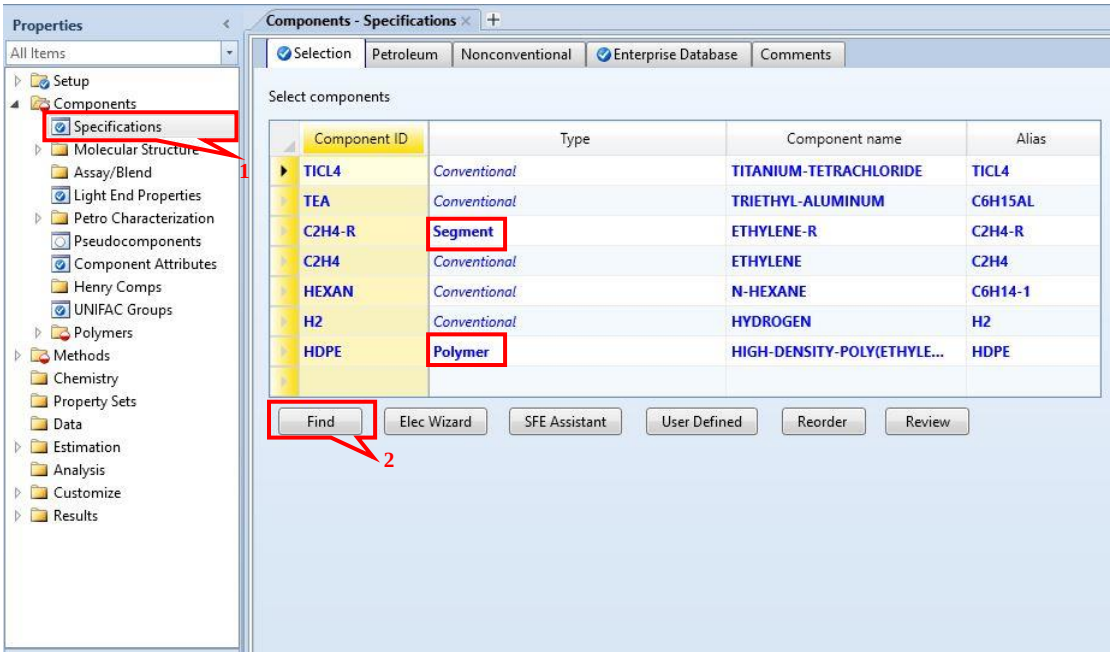


Component specification

2. In the *Data Browser*, find **Component Specification** through root *Components*/*Specifications*, define include all the involved components in the simulation. The component ID is what you see in your input and output sheets of the software. So, you can change these IDs as shown below. Also select **polymer** and **segment** as type for **HDPE** and **C2H4-R**, respectively.

Hint!

C_2H_4-R refers to the undeveloped polymer chain at the end of which is a vacant site for reaction and allows the monomer to bind and the polymer chain to propagate.

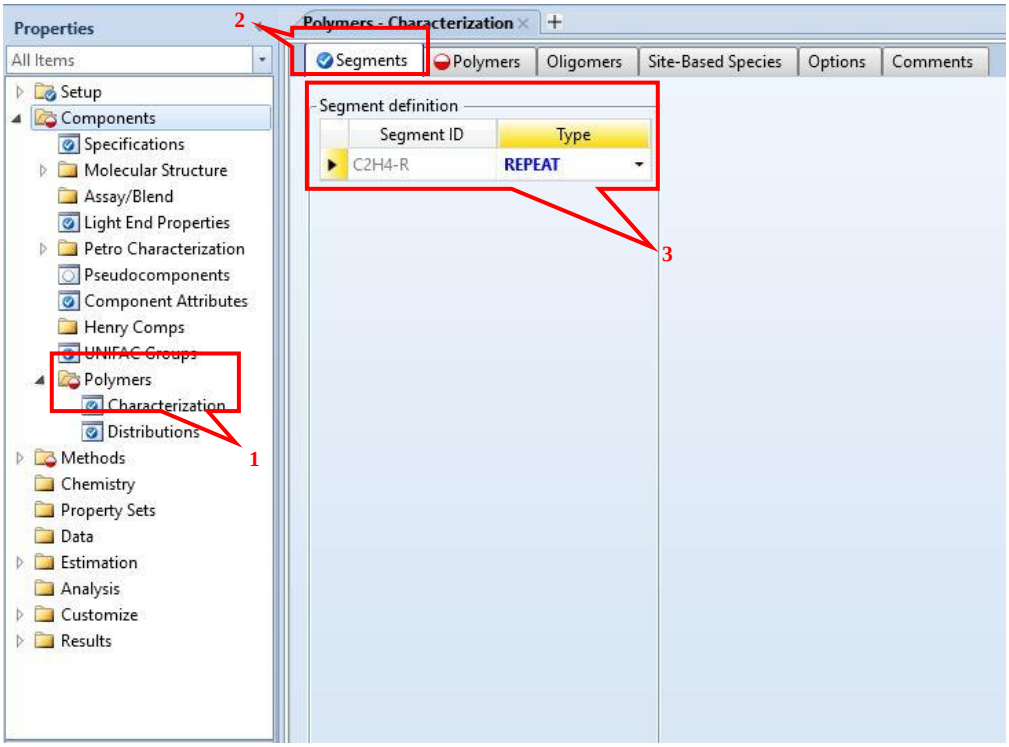


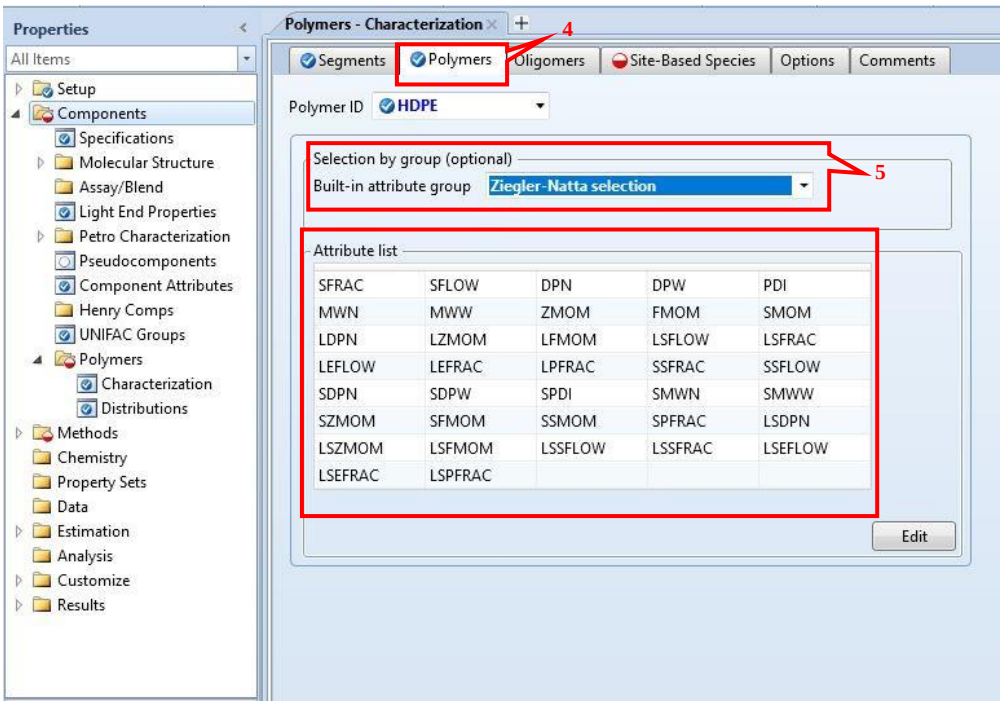
Polymers characterization

3-1. In the *Data Browser*, find **Polymers-characterization** through root *Components/Polymers/Characterization*. In the **Segment** tab, select **C2H4-R** as the **Repeat** unit. Use this sheet to specify the type of all polymer and oligomer segments. Segments are the building blocks that participate in the polymer or oligomer chain. Segments can be repeated units, end groups, or branch points attached to three or four branches.

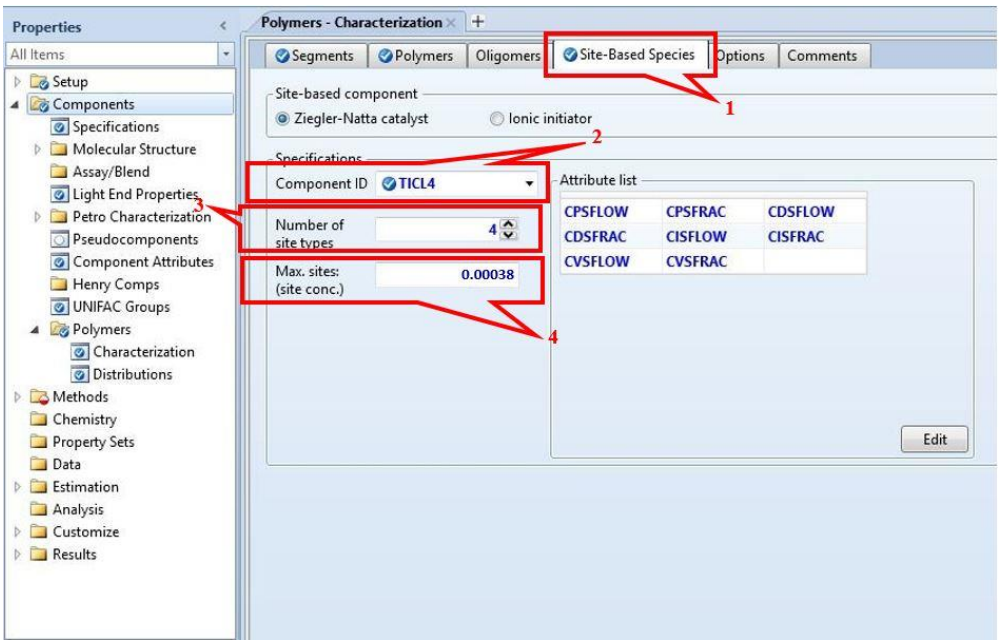
3-2. In **Polymers** tab, select the properties or component attributes that Aspen should tracked for the produced polymers. Component attributes keep track of polymer properties such as degree of polymerization, molecular weight, copolymer composition, etc. To do this, select the **Ziegler-Nata Selection** in the **Built-in attributes group** section. You will see a list of catalyst attributes below it. Site based component attributes are also available to simulate multi-site type Ziegler-Natta catalyst

polymerization. Composite attributes are summed over all site types. They represent the average properties of the polymer.





3-3. In **Site-Based Species** tab, specify the structure and activity of site-based catalytic species such as coordination catalysts and ionic initiators. Polymerization reactions such as Ziegler-Natta polymerization and Ionic polymerization use multi-site catalytic species. Each site is responsible for producing polymer chains with different characteristics. Specify the number of site types in the Number of sites for the catalyst. You must also specify the moles of sites per gram of catalyst (as shown in the figure below).



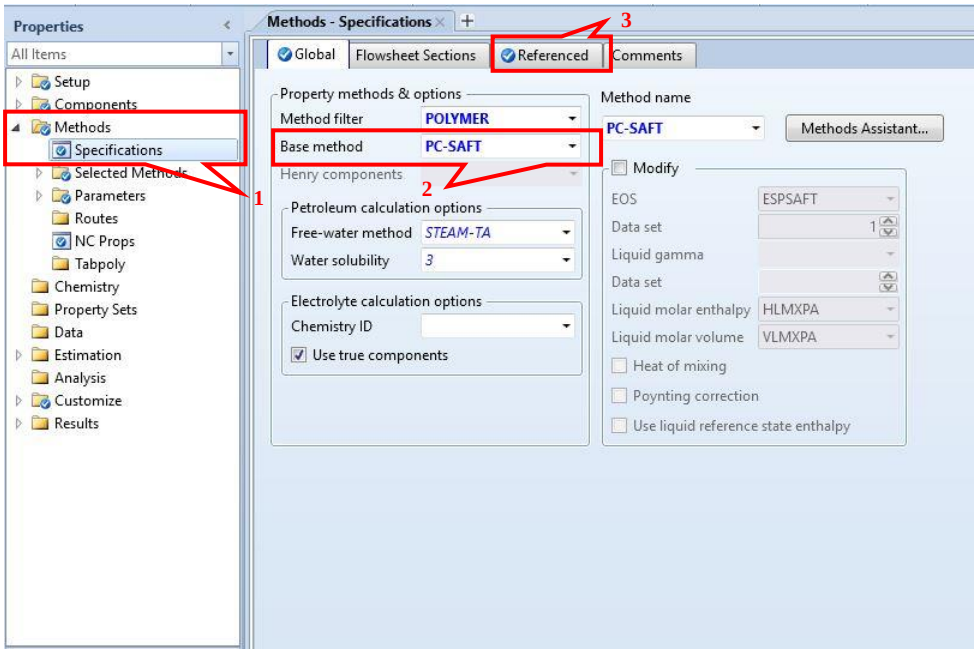
Hint!

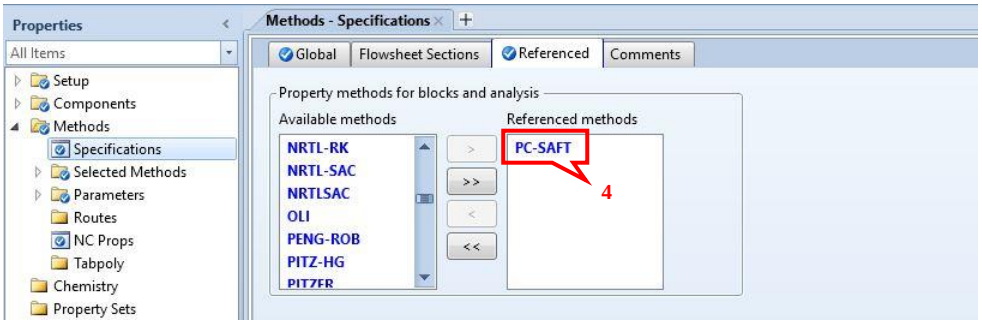
Component attributes are used to track multi-site heterogeneous polymerization (Ziegler-Natta) catalyst site activity, in terms of mole flow and the fraction of potential, inhibited, vacant, and dead sites. The occupied sites are not tracked since that information may be obtained from the live polymer zeroth moment of chain length distribution.

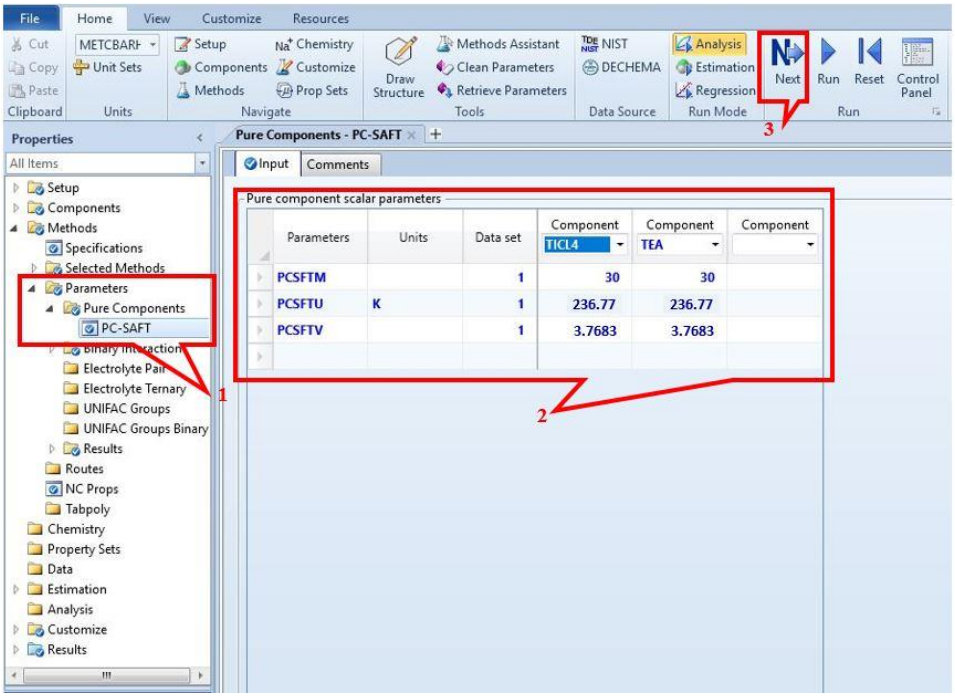
Property model specification

4-1. In the *Data Browser*, find **Properties Specification** through root *Properties/Methods/Specification* form. In **Global** tab, Select **PC-SAFT** as the base method and in **Referenced** tab, add **PC-SAFT** as the Referenced methods from Available methods list.

4-2. The PC-SAFT parameters for components $TiCl_4$ and TEA are not available in the data bank. You need to define the required scalar parameters of these components. Go to *Properties/Methods/Parameters/Pure Components,* add a **New** pure component scalar parameter (name it "PC-SAFT") and enter the values of each parameter according to what is shown in the figure. Then click next button (**N→**) to review the binary interactions for this EOS.


Properties
All Items
Setup
Components
Methods
Specifications
Selected Methods
Parameters
Routes
NC Props
Tabpoly
Chemistry
Property Sets
Data
Estimation
Analysis
Customize
Results
Methods - Specifications
Global
Flowsheet Sections
Referenced
Comments
Property methods & options
Method filter
POLYMER
Base method
PC-SAFT
Henry components
Petroleum calculation options
Free-water method
STEAM-TA
Water solubility
3
Electrolyte calculation options
Chemistry ID
Use true components
Method name
PC-SAFT
Methods Assistant...
Modify
EOS
ESPSAFT
Data set
1
Liquid gamma
Data set
Liquid molar enthalpy
HLMXPA
Liquid molar volume
VLMXPA
Heat of mixing
Poynting correction
Use liquid reference state enthalpy
1
2
3

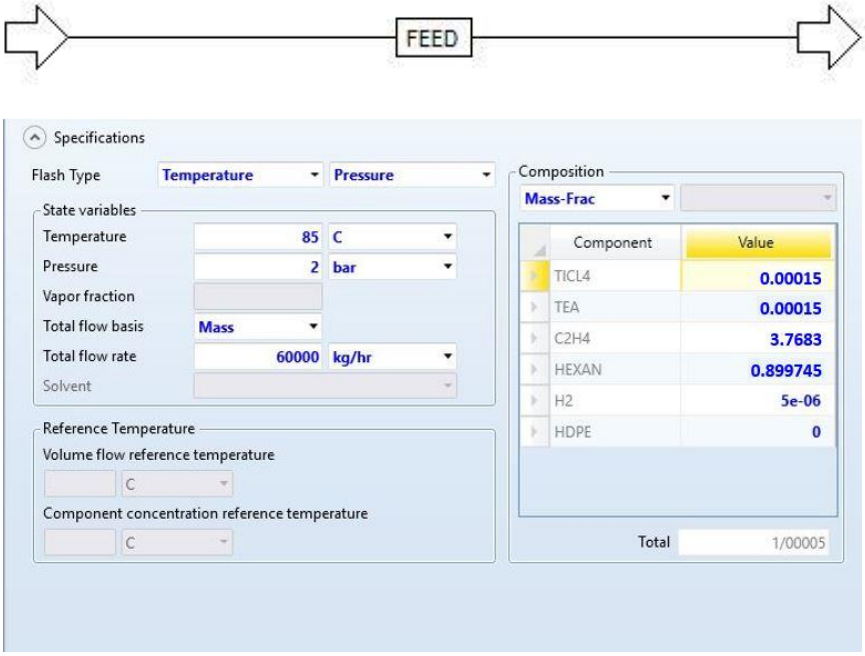

Properties
All Items
Setup
Components
Methods
Specifications
Selected Methods
Parameters
Routes
NC Props
Tabpoly
Chemistry
Property Sets
Methods - Specifications
Global
Flowsheet Sections
Referenced
Comments
Property methods for blocks and analysis
Available methods
Referenced methods
NRTL-RK
NRTL-SAC
NRTLSAC
OLI
PENG-ROB
PITZ-HG
PITZER
PC-SAFT
>
>>
<
<<
4



Flowsheet development

FEED Stream

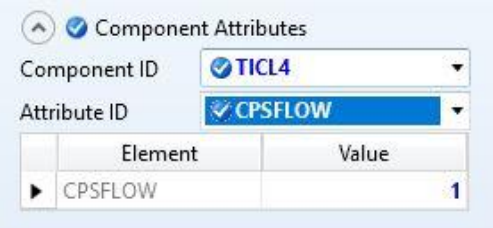
5. From **Module Palette**, drag a material stream into the **Main flowsheet window** and rename it (using Ctrl+M) to **FEED**. Double click on this stream to open stream specification form. Complete the feed condition as shown here.



6. In the **Components Attributes** section, enter the following values for each of the catalyst attributes:

Table2. The values of the components Attributes [1]

Attributes ID	Value	Unit
CPSFLOW	1	[mol]
CPSFRAC	1	[-]
CVSFLOW	0	[mol]
CVSFRAC	0	[-]
CISFLOW	0	[mol]
CISFRAC	0	[-]
CDSFLOW	0	[mol]
CDSFRAC	0	[-]



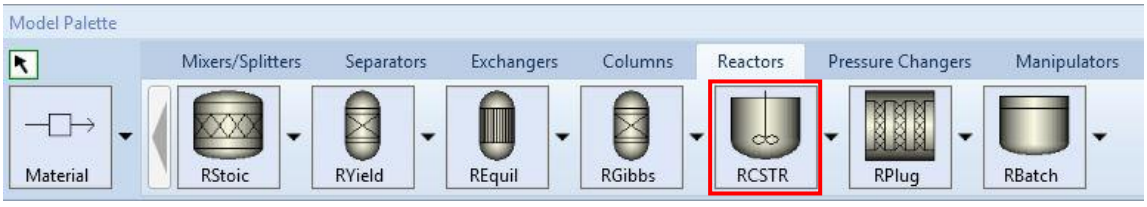
Note

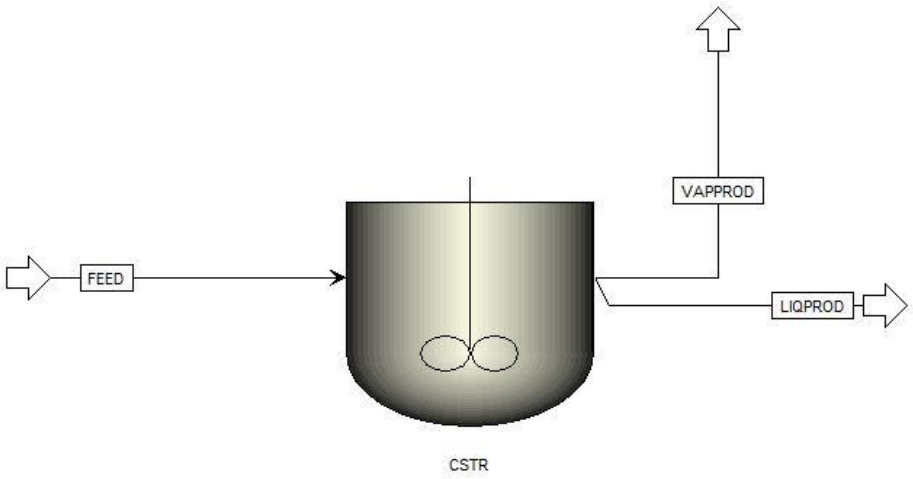
Component attributes are used to track multi-site heterogeneous polymerization (Ziegler-Natta) catalyst site activity, in terms of mole flow and fraction of potential, inhibited, vacant, and dead sites. The site types are defined as follows:

- Potential Sites - sites that are not yet activated.
- Vacant Site – sites that are activated without a growing polymer attached.
- Inhibited Sites - activated sites that are temporarily in inactive state.
- Dead Sites - sites that have permanently lost their catalytic activity.
- Occupied Sites - activated sites with a growing polymer attached.

Reactor

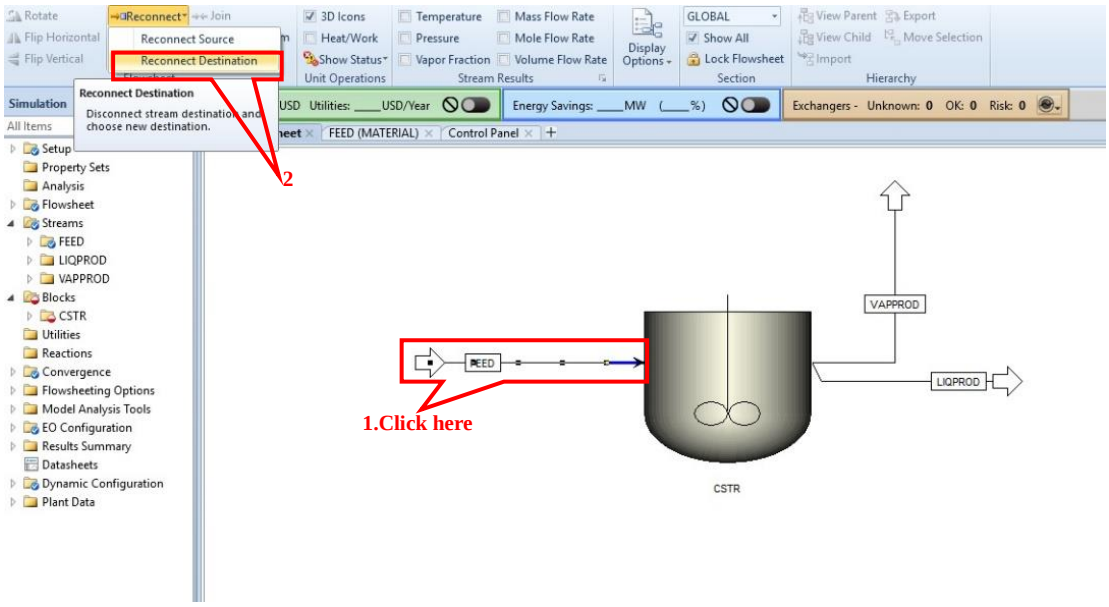
7. From **Module Palette, Reactor** tab, drag a **RCSTR** and connect the FEED stream to its inlet port. Drag two material streams into the flowsheet and connect them to the **Product** ports (one as the slurry phase outlet stream and the other as the vapor phase outlet stream). Rename them to **LIQPROD** & **VAPPROD**, as shown:



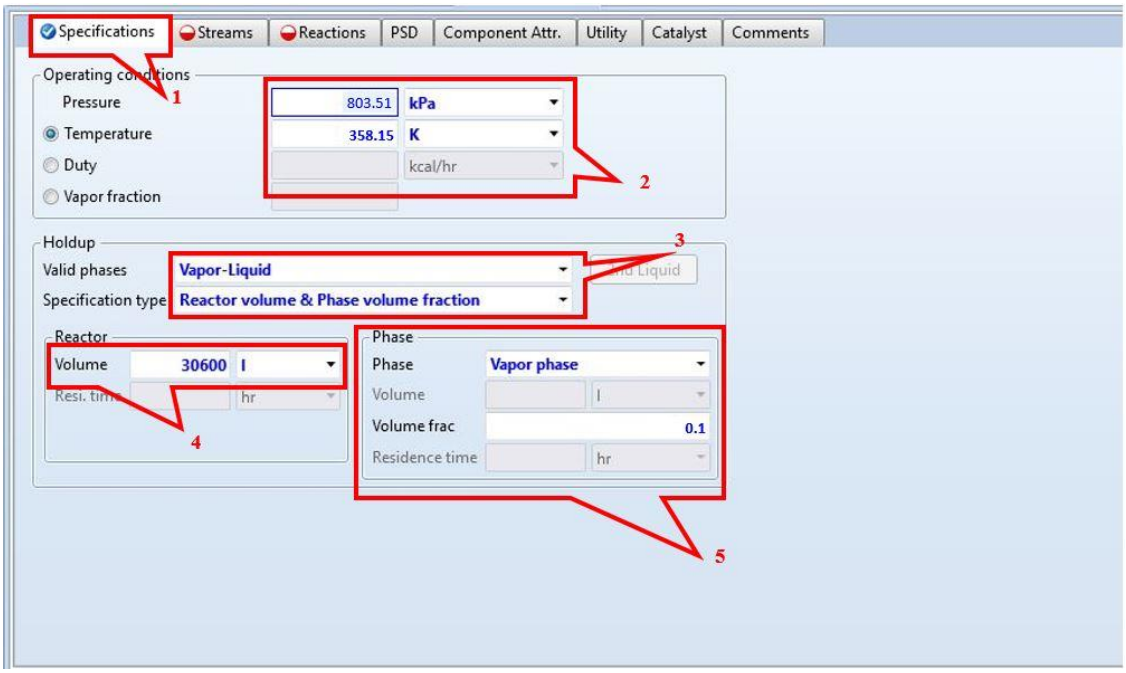


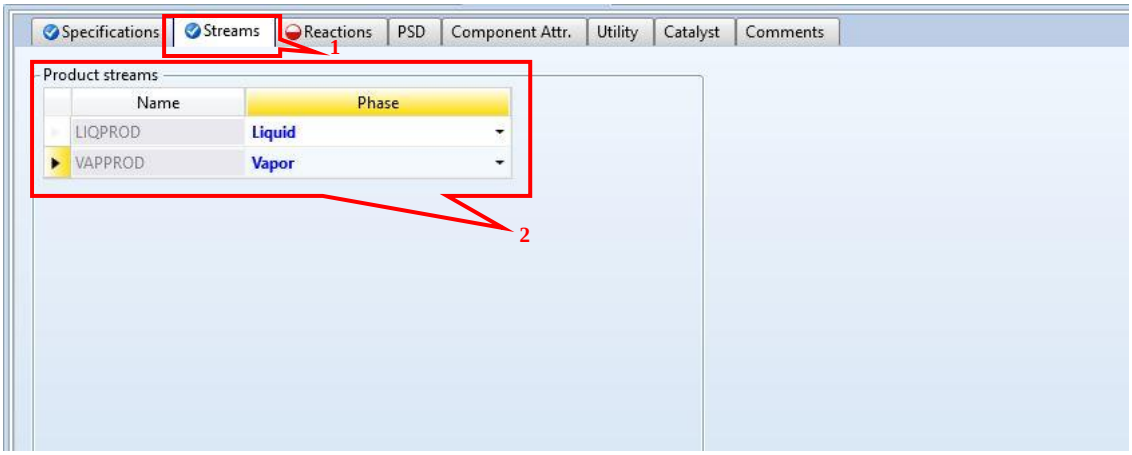
Hint!

To connect the **FEED** stream to the **CSTR**, right-click on **FEED** and select the **Reconnect Destination** to set the stream destination to the reactor inlet.

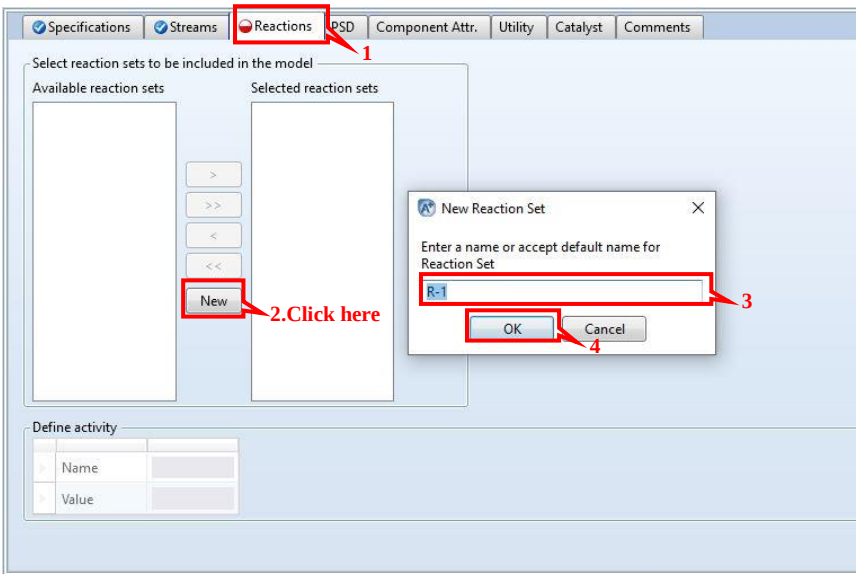


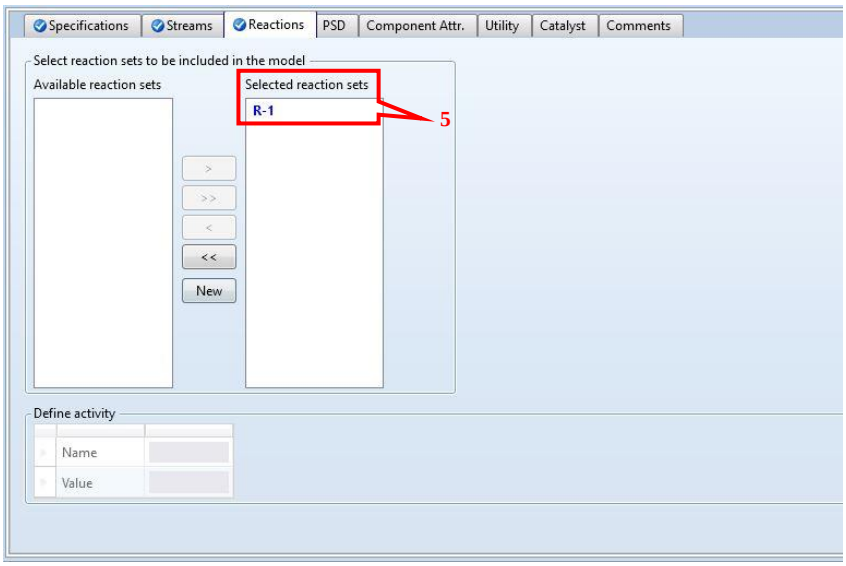
8. Double click on the **CSTR** to open the reactor specification form. Complete the operating conditions and output stream phases here. In **Specifications** tab, select **Vapor-liquid** mode as the **Valid phases** and enter the value **0.1** for the **volume fraction** of the vapor phase. Then, in **Streams** tab select liquid and vapor phase for **LIQPROD** and **VAPPROD**, respectively.



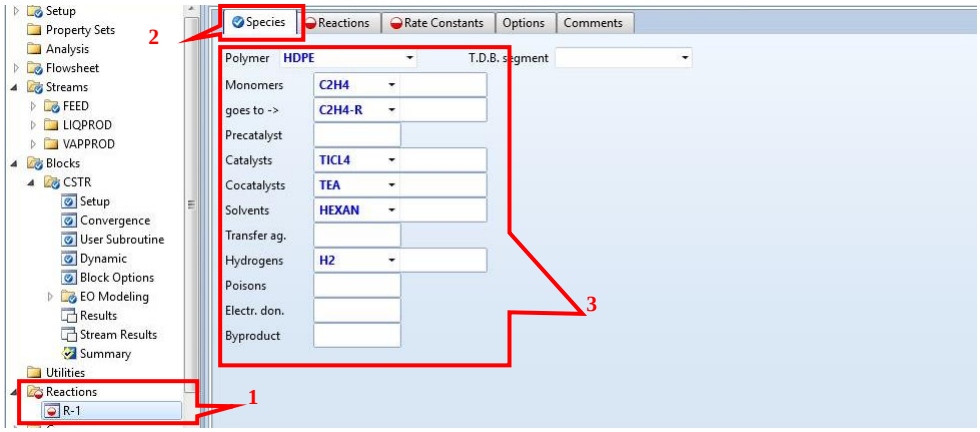


9. In **Reactions** tab, click **New** button and enter R-1 for this new reaction set. Then, Select **ZIGLER-NAT** from the menu and then move **R-1** to **Selected Reaction Sets**.





10-1. In the *Data Browser*, Go to *Reactions/R-1*, and fill in the blanks in **Species** tab with the proper values as shown below.

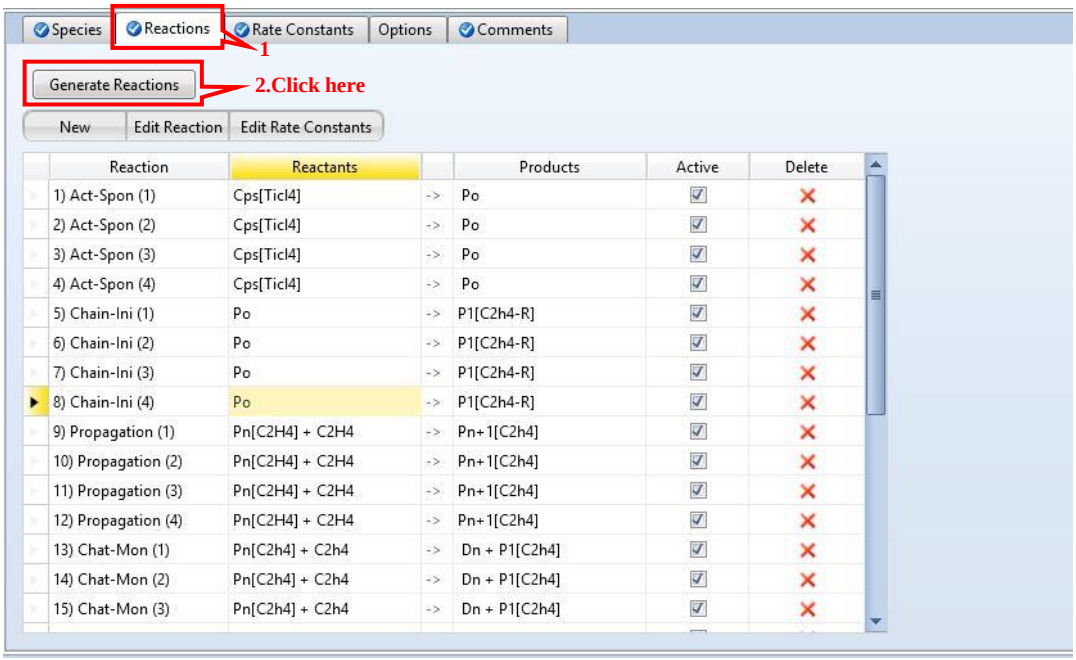


10-2. In **Reactions** tab, click on **Generate Reactions** button. Then, remove the reactions that are not listed in Table 3.

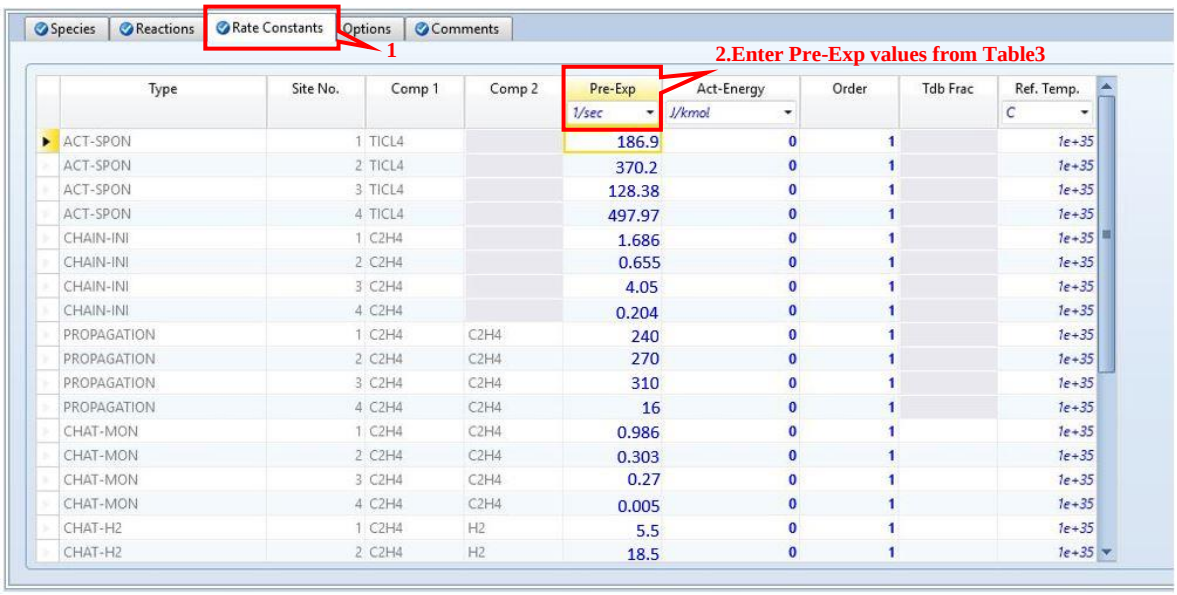
Table 3. Literature Data of Pre-Exponential Kinetic Rate Constants [2]

Reaction Name	Reaction Types	Reactants	Site1	Site2	Site3	Site4	Unit
Spontaneous activation	ACT-SPON	Cps[$TiCl_4$]	186.9	370.2	128.38	497.97	[L/mol.s]
Chain initiation	CHAIN-INI	Po	456.3	1.686	0.655	4.05	[L/mol.s]
Propagation	PROPAGATION	Pn[C_2H_4] + C_2H_4	240	270	310	16	[L/mol.s]
Chain transfer to monomer	CHAT-MON	Pn[C_2h_4] + C_2h_4	0.986	0.303	0.27	0.005	[L/mol.s]
Chain transfer to hydrogen	CHAT-H2	Pn[C_2h_4] + H_2	5.55	18.5	0.002	2.7e-06	[L/mol.s]
Chain transfer to Spontaneous	CHAT-SPON	Pn[C_2h_4]	0.002	0.001	0.00035	8.7e-10	[L/mol.s]
Spontaneous deactivation	DEACT-SPON	Po/Pn	0.002	0.00098	0.00034	0	[L/mol.s]

* The order of chain transfer to hydrogen was considered one instead of the original value of 0.5 in the reference.

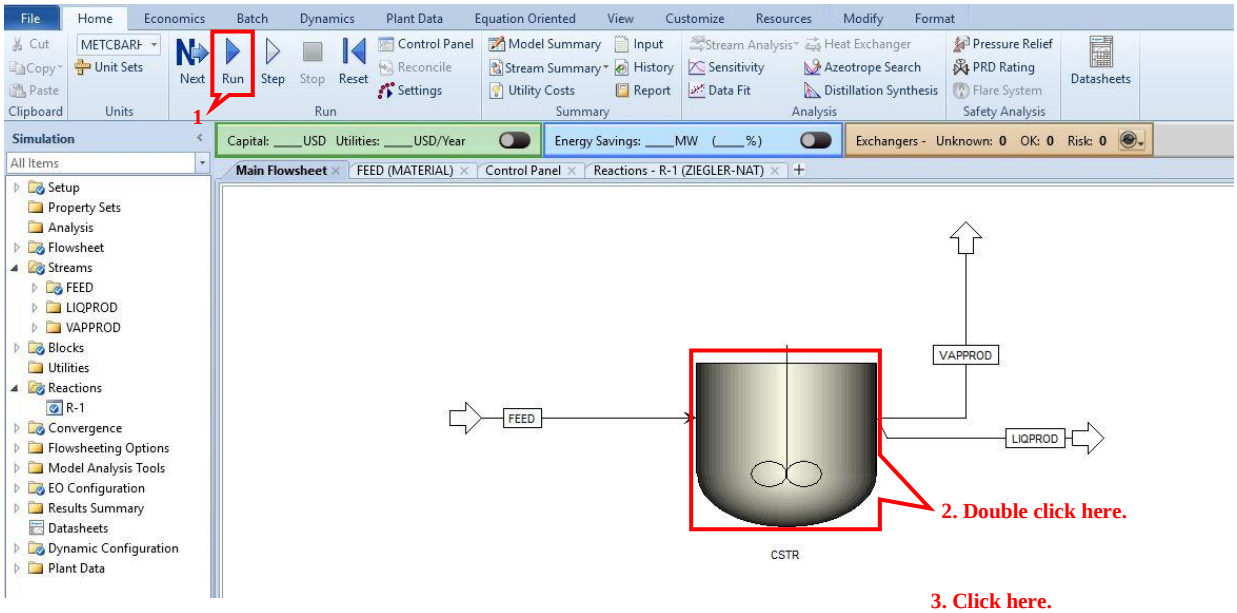


10-3. In **Rate Constant** tab, Enter the values in **Pre-Exp** column using Table 3. Set the unit of these values to **1/sec**.



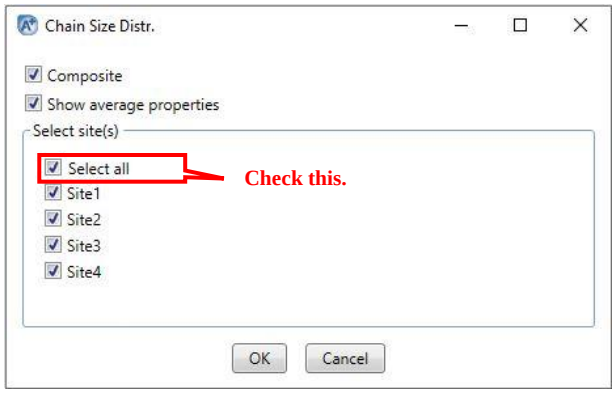
Type	Site No.	Comp 1	Comp 2	Pre-Exp 1/sec	Act-Energy J/kmol	Order	Tdb Frac	Ref. Temp. C
ACT-SPON	1	TICL4		186.9	0	1		1e+35
ACT-SPON	2	TICL4		370.2	0	1		1e+35
ACT-SPON	3	TICL4		128.38	0	1		1e+35
ACT-SPON	4	TICL4		497.97	0	1		1e+35
CHAIN-INI	1	C2H4		1.686	0	1		1e+35
CHAIN-INI	2	C2H4		0.655	0	1		1e+35
CHAIN-INI	3	C2H4		4.05	0	1		1e+35
CHAIN-INI	4	C2H4		0.204	0	1		1e+35
PROPAGATION	1	C2H4	C2H4	240	0	1		1e+35
PROPAGATION	2	C2H4	C2H4	270	0	1		1e+35
PROPAGATION	3	C2H4	C2H4	310	0	1		1e+35
PROPAGATION	4	C2H4	C2H4	16	0	1		1e+35
CHAT-MON	1	C2H4	C2H4	0.986	0	1		1e+35
CHAT-MON	2	C2H4	C2H4	0.303	0	1		1e+35
CHAT-MON	3	C2H4	C2H4	0.27	0	1		1e+35
CHAT-MON	4	C2H4	C2H4	0.005	0	1		1e+35
CHAT-H2	1	C2H4	H2	5.5	0	1		1e+35
CHAT-H2	2	C2H4	H2	18.5	0	1		1e+35

11. Click **Run** button (▶) from **Home** tab or press **F5** to run the simulation. Then Double click on the **CSTR** block to see the results. From the top ribbon, in the **plot** section, select the **Chain Size Distribution** to plot the size distribution of each site and combined sites.

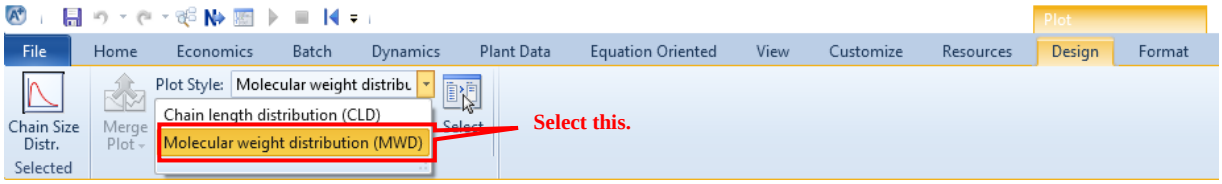


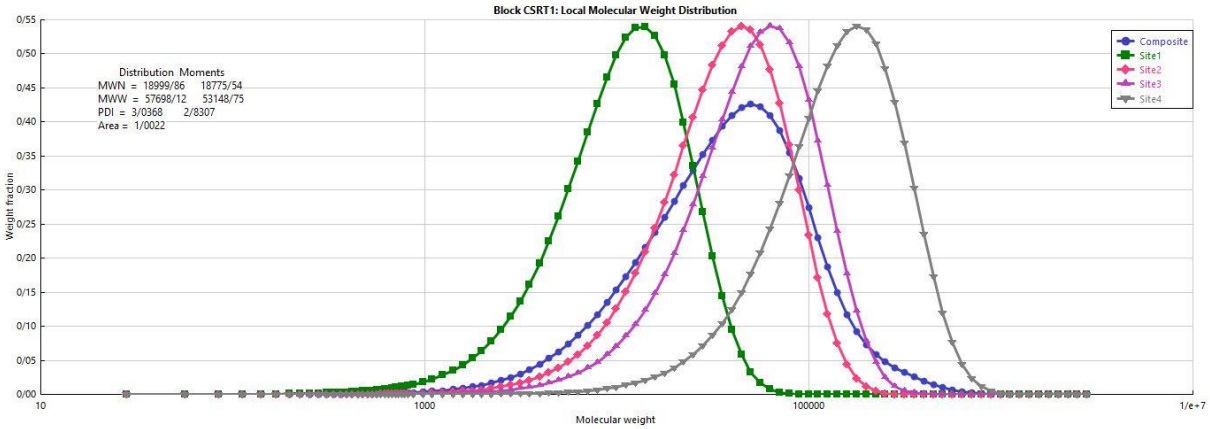
Results

12. Check the **Select All** to show the molecular weight distribution and chain size distribution of all active sites.



13. In the design tab, select **Molecular weight distribution (MWD)** to plot data.

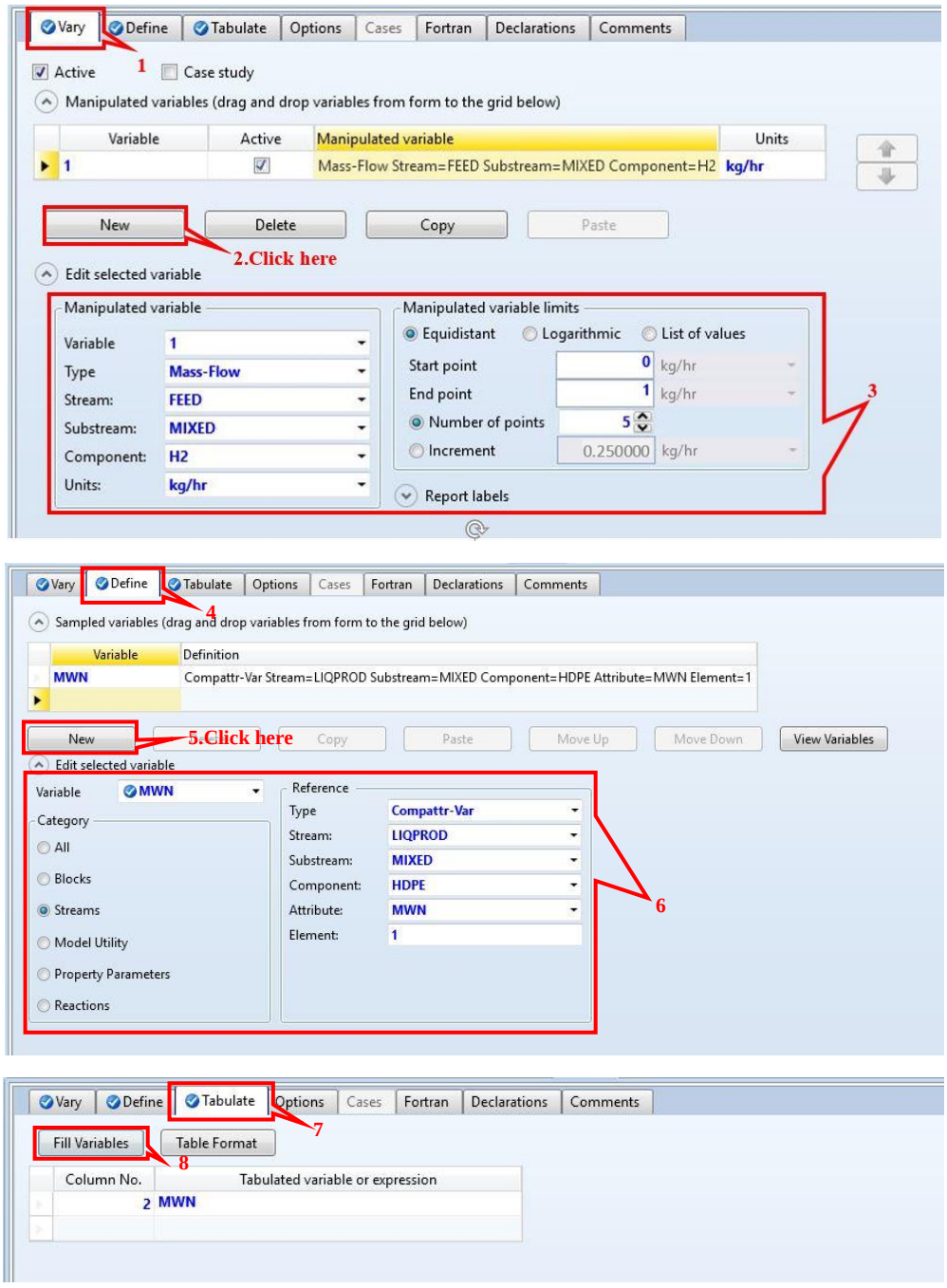




The above figure shows the normalized molecular weight distribution (MWD) for HDPE polymer **CSTR**, in the outlet stream based on two calculation methods for average molecular properties: instantaneous distribution and moments of distribution. Notice that MWW = MWN × PDI. For more information on molecular weight distribution properties, see **APPENDIX**.

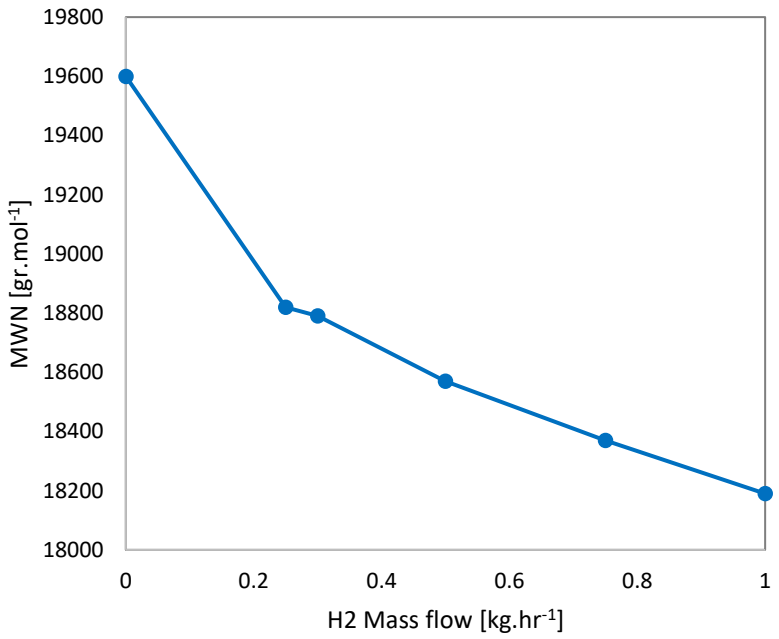
Sensitivity analysis

A sensitivity analysis was carried out to see the effect of H_2 flow rate in the **FEED** stream on the HDPE polymer properties such as MWN and MWW. The following figure, shows **Vary** and **Define** tab setup form of the sensitivity analysis tool in Aspen. The mass flow rate of H_2 is varied from 0 to 1 kg/h. **MWW** and **MWN** are defined as **Compattr-Var** in **LIQPROD** stream (you can find sensitivity analysis tool in path *Data Browser/Model analysis tool/Sensitivity*).

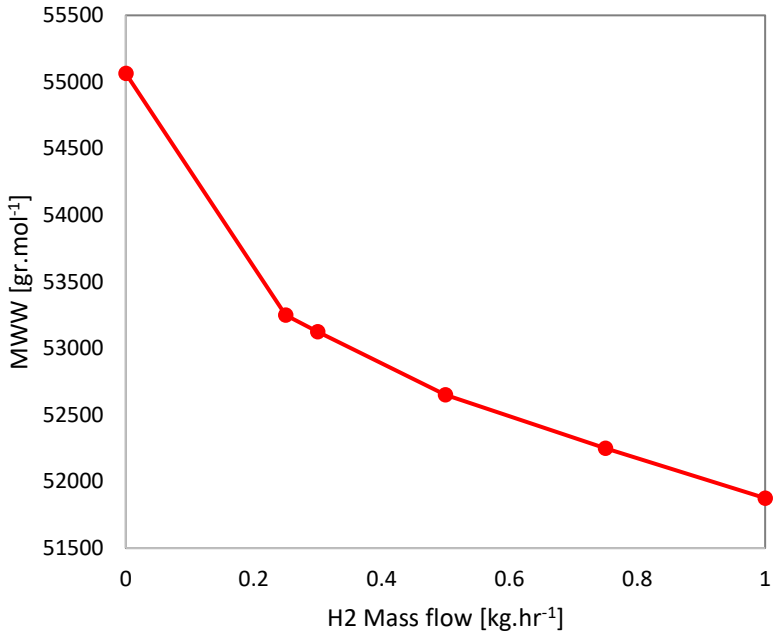


The following two figures show the variations of **MWN** and **MWW** as functions of H_2 flow rate in the **FEED** stream. Notice that both MWN and MWW decrease as H_2 flow rate is increased, indicating that

H_2 competes with the propagation of repeat unit C_2H_4 and prematurely terminates active site propagation.



(a)



(b)

References

[1] K. Al-Malah, *Aspen plus*, 1st ed. USA: John Wiley & Sons, Inc., 2016, pp. 325-360. Available: 10.1002/aic.14527 [Accessed 22 November 2020].

[2] C. Zhang, Z. Shao, X. Chen, Z. Yao, X. Gu and L. Biegler, "Kinetic parameter estimation of HDPE slurry process from molecular weight distribution: Estimability analysis and multistep methodology", *AIChE Journal*, vol. 60, no. 10, pp. 3442-3459, 2014. Available: 10.1002/aic.14527 [Accessed 22 November 2020].

APPENDIX

The number average molecular weight (MWN) and weight average molecular weight (MWW)

The average properties of the polymer chain can be calculated as ratios of the moments. The number-average degree of polymerization (DPN) is the ratio of the first to the zeroth moments, λ_1/λ_0. On the other hand, the weight-average degree of polymerization (DPW) is the ratio of the second to the first moments, λ_2/λ_1. In general, for a polymer with a chain length distribution, the n^{th} moment is given by:

$$\lambda_m = \sum_{n=1}^{N} n^m Q_n \qquad \text{A-1}$$

where

λ Moment

m Moment order

n Chain length or degree of polymerization

Q_n Number of moles of polymer of length n

The polymer average chain length and weight properties are then calculated as follows:

DPN=Number-Average degree of polymerization=$\frac{\lambda_1}{\lambda_0}=\frac{FMOM}{ZMOM}$ A-2

DPW=Weight-Average degree of polymerization=$\frac{\lambda_2}{\lambda_1}=\frac{SMOM}{FMOM}$ A-3

PDI=Poly dispersity index=$\frac{DPW}{DPN}=\frac{\left(\frac{\lambda_2}{\lambda_1}\right)}{\left(\frac{\lambda_1}{\lambda_0}\right)}=\frac{(\lambda_2\times\lambda_0)}{(\lambda_1)^2}=\frac{(SMOM\times ZMOM)}{(FMOM)^2}$ A-4

MWN=Number-Average molecular weight=$DPN\times\overline{M}_{segment}$ A-5

MWW=Weight-Average molecular weight=$DPW\times\overline{M}_{segment}$ A-6